

## 6. AGENT STABILITY UNDER STORAGE AND DISCHARGE RESIDUE

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### 6.1 Agent Stability Under Storage

Halon 1301 is known to be stable in metal containers for many years. Any by-products do not affect its fire suppression effectiveness or result in an unacceptable residue. For candidate replacement chemicals, comparable data are needed, reflecting the storage conditions of elevated temperature and pressure. Significant losses in fire suppression effectiveness and increases in toxicity are possible if the extinguishing agent degrades during storage. Thus, stability during the multi-year storage environment is an important concern.

The storage environment fosters conditions which may have an adverse effect on the stability of halon replacements. Stored chemicals may engage in oxidation-reduction reactions, hydrolysis, and other corrosive interactions with metal cylinders. They are also subject to unimolecular decomposition and attack by reactive impurities in the agent. Water and oxygen, for example, will sorb to surfaces of cylinders and transfer lines and can never be completely excluded. These sources of instability, along with the possibility of catalytic interactions with the cylinder walls, can promote the evolution of undesirable products and a concomitant loss of fire suppression effectiveness. Toxicity and corrosiveness are particularly important concerns with respect to halogenated compounds, due to the tendency to liberate hydrogen halide in the process of degradation.

NIST Technical Note 1278 (Gann *et al.*, 1990) details a screening test for the stability of chemicals, with the purity of the chemical determined by infrared spectral analysis. This test involves storing the candidate in a carbon-steel cylinder for two days at a temperature of 170 °C (338 °F). The infrared spectra of the original and "aged" samples are compared. Although appropriate for a screening procedure, promising candidate agents need a more rigorous examination.

In this project, samples of each of the 12 candidate agents were evaluated in pressurized cylinders. It was presumed that  $\text{NaHCO}_3$  is stable under the likely storage temperatures and pressures. In order to allow for potential interactions analogous to actual storage conditions, a measured amount of metal (with separate tests for each candidate cylinder metal) was introduced into the containers prior to the experiments. The vessel and its contents were stored in an oven at elevated temperature for 28 days. After cooling to ambient conditions, an infrared spectrum of the aged sample was compared to a spectrum of the original sample. Degradation of the sample would be indicated by a systematic decrease in the absorbance of peaks attributable to the agent and/or the appearance of new peaks in the IR spectrum of the aged agent.

**6.1.1 Selection of Experimental Technique.** The most reliable way to assess storage stability is to determine the shelf life of each chemical by monitoring its degradation in the actual storage environment. Existing ASTM test methods for assessing the storage stability of aircraft cleaning compounds are available (ASTM, 1987a and 1987b). After storage at specified conditions for 12 months, samples are inspected for signs of corrosion and sediment formation, and their performance is tested

against contract specifications. For evaluation of potential halon replacements, such long term storage is only practical for evaluating a near-final selection of agents. For the current project, an alternative approach must be taken.

The temperature dependence of potential reactions can be dramatic. For example, the rate of a chemical reaction with an activation energy of 126 kJ/mole, which is reasonable for catalytic degradation, increases by almost a factor of  $10^9$  over the temperature range from 25 to 225 °C. The ASTM test method for distillate fuels uses this phenomenon to accelerate aging in samples stored from 4 to 24 weeks at 43 °C. The elevated temperatures used in these test accelerate aging and make it possible to complete long-term stability assessments in a time frame of weeks rather than years.

The strategy of using temperature to study stability is also the basis of differential thermal analysis (DTA). This technique is frequently used to study phase transitions and assess thermal stability in liquids and solids (Wendlandt, 1964). In DTA, thermocouples are used to monitor the temperature difference between the sample and an inert reference material as a function of increasing temperature. A thermal event is signaled by a peak in the trace of voltage versus temperature and is indicative of a reaction in the sample. DTA is useful for measuring transition temperatures and for determining the signs of observed enthalpy changes. An ASTM standard test method for assessing thermal stability using DTA (E 537-86) is performed by observing the temperature changes which result from heating the sample from room temperature to about 500 °C. In performing this test, the investigator makes note of all enthalpy changes, the temperatures at which these transitions occur, whether they are exothermic or endothermic, and the effects of changing the atmosphere in the test cell. The criteria for thermal stability is the absence of a reaction.

Neither DTA (or the related differential scanning calorimetry) are appropriate for the current study. These techniques are typically applied to detect chemical reactions and phase transitions in solids. They would be difficult, if not impossible, to apply to potential halon replacements, which are, almost exclusively, gases and volatile liquids. More importantly, they measure thermal, as opposed to storage stability. The presence of reactive impurities or heterogenous catalysis in the storage environment cannot be determined by studying pure samples of the agent alone.

Actual storage at elevated temperatures for some period of time is thus desirable. Degradation can be monitored via conventional analytical techniques, such as gas chromatography (GC) (Grob, 1977) or infrared spectroscopy (IR) (Willis, *et al.*, 1987).

A GC consists of a heated injection port connected to a column which is coated with an adsorbent material called the stationary phase. Mixtures are transported through the column by an inert gas. The components are separated on the basis of the amount of time they require to traverse the length of the column. Retention times in the column increase with the affinity of the component to the stationary phase. A detector is positioned so that it can respond to the individual components as they are sequentially eluted from the column. Ideally, the chromatogram, which is a plot of detector response versus retention time, consists of a series of well-resolved peaks, each of which corresponds to a pure compound. In practice, however, co-elution of components is an important concern which must be addressed by temperature programming and careful selection of the stationary phase. Accurate measurements of the concentrations of identified mixture components are frequently made using a GC equipped by an ionization detection or electron capture detector. To make definitive compound identifications, the GC is often paired with a mass spectrometer.

Chemical analysis by IR spectroscopy is based on the assumption that the IR spectrum of a compound is sufficiently unique to identify it. An IR spectrum is obtained by measuring the ratio of the intensity of IR radiation which passes through the sample,  $I$ , to the intensity of the incident radiation,  $I_0$ , as a function of frequency. Concentrations of individual components are quantified by applications of Beer's law

$$C_i = \left[ \frac{A_i(\nu)}{A_r(\nu)} \right] C_r, \quad A(\nu) = -\log \frac{I(\nu)}{I_o(\nu)}, \quad (1)$$

where the subscript  $r$  indicates known values obtained from a reference sample. IR spectroscopy is extremely versatile in the sense that almost all compounds, with the notable exception of single atomic and homonuclear diatomics, are IR active. In principle, IR analysis makes it possible to monitor the degradation of each candidate and identify the corresponding products from a sample before and after comparison of the spectra. In practice, IR analysis can suffer from overlapping peaks in a spectrum similar to problems with gas chromatography. In addition, quantitative determination of degradation products require either pre-existing spectra for comparison (libraries of spectra for common materials are commercially available) or available reference samples.

GC is much more sensitive than IR. The major disadvantage is the considerable effort and expense involved in column preparation and selection. This situation is exacerbated by the need to use different columns to resolve a wide variety of alternative chemicals from their degradation products. In addition, since it was expected that the additional sensitivity afforded by GC would not be needed in most cases (most of the compounds were expected to be stable), the speed, cost, and acceptable resolution of IR spectroscopy made this approach the best alternative for the screening tests conducted. For longer-term studies, to be performed once the list of acceptable chemicals has been reduced to a few alternatives, IR studies can be supplemented with GC analysis as appropriate.

Since the agents may interact with metal storage cylinders during long term storage, it is important to evaluate the agents in the presence of a variety of metals which may be encountered during typical use. Table 1 shows the metals selected for the current study. Although the primary interest is in storage cylinder materials, additional materials which may come in contact with the agents for extended periods of time were included. Ideally, containers constructed of each material would be used for agent storage during the study. However, cost and availability of containers made from the eight metals necessitated the use of metal coupons inside an inert container. In this approach, an amount of metal with surface area roughly equal to the storage cylinder was introduced into teflon-lined stainless steel cylinders prior to agent filling. With new metal samples for each experiment, this also eliminated potential longer-term degradation of the metals over multiple experiments.

**6.1.2 Experimental.** A total of thirteen agents were screened for their long-term storage stability (twelve candidate replacement agents and halon 1301). Each agent was exposed to fixed amounts of eight different metals at elevated temperature and pressure. Testing conditions dictated that the exposure temperature be fixed at 149 °C, and that the room temperature fill pressure be 4.13 MPa (600 psia). In order to assure that the storage cylinder pressure not exceed the pressure rating on the cylinder or valve when exposed to the elevated temperature, a conservatively low amount of agent was placed in each cylinder. The cylinders were filled with agent up to a maximum pressure of the saturation vapor pressure of the agent at room temperature (in the case of the gaseous agent, up to a fixed pressure). Nitrogen was then added to achieve the final pressure. Since small amounts of additional liquid would vaporize at the elevated temperature only a single phase would exist anyway, though a significant pressure increase would be observed. The effect of the system pressure on degradation was not explored, but is thought to be small.

Eight different metals were chosen to be exposed to the agents for the screening. The metals were introduced into the cylinders as coupons 10.2 cm long, 0.8 cm wide, and 0.2 cm thick. The number of coupons was fixed at 30 for each cylinder because that amount is approximately the

Table 1. Metals used in Agent Stability Study

Metal	Major Constituents	Typical Use
Nitronic-40 (21-6-9 Stainless)	Cr Mn Ni Fe	Pressure vessel
304 Stainless	Cr Ni Fe	Pressure vessel, pressure vessel fitting, gage fitting, and diagnostic devices
AM 355 Stainless	Cr Mo Ni Fe	Outlet closure
4130 Alloy Steel	Cr Mn Si Fe	Pressure vessel
13-8 Mo Alloy Steel	Al Cr Mo Ni Fe	
Inconel 625	Cr Fe Mo Ni	Bourdon tube
6061-T6 Aluminum Alloy	Al Si Fe Mg	Compression gasket, fill fitting
CDA 172 Cu-Be Alloy	Cu Be	Bourdon tube, outlet closure

surface area of the interior of the cylinder. Overlapping of the coupons in the cylinder effectively decreased the exposed surface area, but this decrease, though not calculated, should be similar for all tests.

**6.1.2.1 Test Preparation.** The storage cylinders were constructed of stainless steel, lined with polytetrafluoroethylene (PTFE), and had a 1000 ml capacity. All new cylinders were assembled with high temperature/high pressure stainless steel valves and end plugs, then heated to 149 °C (300 °F) for at least 48 hours with the valves completely open. For re-used cylinders, the heating time was cut to 24 hours.

The metal coupons were immersed in dichloromethane solvent and stirred around to remove any oil residue and markings on the surfaces. The coupons were removed from the solvent, stripped with clean paper towels, and dried at room temperature. Care was taken to handle the cleaned coupons with gloved hands only. Thirty pieces of each metal were weighed and placed into their respective cylinders. The end plugs threads were wrapped with PTFE tape and tightened. The cylinder valves were opened and the cylinders were heated for at least 12 hours at 149 °C. After the cylinders were removed from the ovens, the valves were closed.

**6.1.2.2 Filling Procedure.** When the cylinders were cool enough to be handled with gloves, they were evacuated to an absolute pressure of less than 20 Pa (0.15 torr). Each evacuated cylinder was weighed. The agents were added and the cylinder was pressurized to the final pressure with nitrogen. The detailed filling procedure is given below.

The filling procedure was designed to insure low levels of contaminant (including room air) and a reasonably accurate measurement of the amounts of material introduced into the cylinder. Highly accurate measurement of amounts of agent and/or nitrogen are not required in this screening method

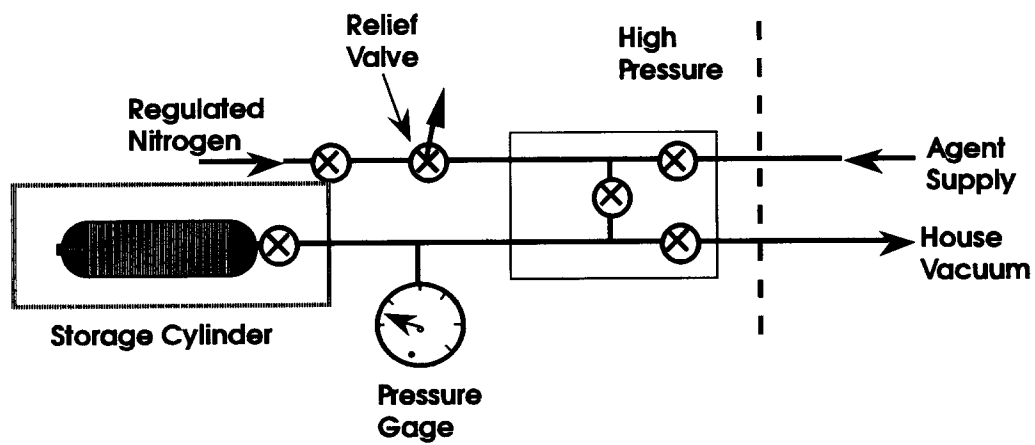


Figure 1. Experimental apparatus for agent filling study.

since it is the change in spectra that was desired. Figure 1 is a schematic of the filling apparatus. It consisted of a three valve manifold, an absolute pressure gage, and filling lines, all constructed from stainless steel and capable of handling high pressures. The lines to the agent tank and the house vacuum were not high pressure rated and were isolated by valves. The following steps outline the filling procedure.

1. The evacuated cylinder was attached to the filling apparatus.
2. The apparatus was evacuated with the house vacuum which was capable of pulling a vacuum down to 34 kPa. Then the valve to the house vacuum was closed.
3. The apparatus was pressurized with nitrogen in excess of 1.4 MPa. The pressure was released through the relief valve.
4. The apparatus was then evacuated again with the house vacuum. Steps 2-4 purge the filling apparatus. After purging the amount of room air in the apparatus was less than 1 % of the original amount. The volume of the filling apparatus is much less than a storage cylinder, so the percentage of air in any filled cylinder was very small (on the order of 0.01 %).
5. The agent inlet valve was opened slowly and the pressure in the apparatus checked (the agent inlet line is pre-charged with agent). At this point if the agent cylinder included a regulator, the delivery pressure could be adjusted. The valve to the cylinder is slowly opened and agent flowed in. Both the inlet valve and the cylinder valve must be opened slowly to avoid the possibility of drawing liquid agent into the apparatus. The system was allowed to equilibrate for one to two minutes, the pressure recorded, and the agent inlet valve closed.

Here we note that the delivery pressure of the agent was, in most cases, the saturation vapor pressure at room temperature of that particular agent. One agent (FC-116) was available as a high pressure gas, and two other agents (HFC-125 and the azeotrope of HFC-32 and HFC-125) had saturation vapor pressures somewhat higher than the other agents, therefore the delivery pressure for these agents was specified to yield a mass of agent delivered to the cylinder close to the mass delivered for most of the other agents.

6. Nitrogen was added to increase the total pressure to nominally 4.20 MPa. This pressure was slightly higher than the prescribed target pressure of 4.13 MPa, but because a small amount of the agent/N<sub>2</sub> mixture was removed from the cylinder for the initial FTIR analysis, a slight decrease in the initial (cold) storage pressure was observed. The total pressure was recorded and the valve to the storage cylinder closed.
7. The pressure was bled from the apparatus and the cylinder disconnected and weighed. At this point, a new cylinder can be connected and filled starting with Step 1 above.

**6.1.2.3 Conduct of the Tests.** Each cylinder was connected to the inlet of the gas cell on the FTIR system. A vacuum of less than 20 Pa was drawn on the gas cell and inlet line up to the cylinder valve. A needle valve was placed in line between the cylinder valve and the gas cell to accurately control the flow of the agent into the gas cell. The agent/N<sub>2</sub> was introduced into the gas cell to an absolute pressure of  $1330 \pm 10$  Pa ( $9.95 \pm .05$  torr). Three spectra were taken for each sample. The cylinders were then re-weighed.

The filled cylinders were placed in the ovens at 149 °C and the time and date were recorded. Periodically, the cylinders were removed and weighed while still hot, then placed back in the oven to check for leakage. It was observed that the valves had to be re-tightened (while hot) after being in the ovens for a day or two. In very few cases was leakage significant, though it appeared that the valves used in this study degraded after some re-use leading to some leaking. In any long term study the valves should be capped to prevent leakage. After 28 days the cylinders were removed from the ovens and allowed to cool before the spectra were taken.

The final spectra were obtained in the same manner as the initial spectra. Comparisons between the initial and final spectra were made.

**6.1.2.4 Exposed metals.** The agent/N<sub>2</sub> mixture was released from each cylinder in an exhaust hood. The end plugs were removed and the metal coupons shaken from the cylinders. The metals were examined visually for changes, wrapped in aluminum foil and retained for reference. The cylinders were then ready for reuse.

**6.1.3 Results.** Table 2 lists the metal mass, agent pressure, calculated agent mass, and initial agent/N<sub>2</sub> pressure and mass before and after storage. In this table, the agent mass was calculated from the agent density at the recorded pressure and ambient temperature (along with the fixed 1000 ml volume of the cylinders). The error in this calculated value is the combination of the uncertainty in the agent pressure reading which is estimated to be  $\pm 0.01$  MPa ( $\pm 2$  psia), deviations of the agent temperature from ambient temperature (at least two minutes were allowed for the system to equilibrate) and the error associated with the equation of state. Here, generalized compressibility charts were used (Balzhiser *et al.*, 1972). The combined uncertainties in the calculated values were not estimated. Uncertainty in the recorded masses depends on the weighing apparatus (agent/N<sub>2</sub> masses were obtained by subtracting the initial mass of the evacuated cylinder with metals in place). Neglecting the cases where obvious leaking occurred, the masses of the agent/N<sub>2</sub> were within  $\pm 5\%$  for any given agent with the exception of FC-31-10. Inspection of the calculated agent masses, and measured agent/N<sub>2</sub> masses for the FC-31-10 indicates that some liquid agent was probably drawn into the cylinder during filling (approximately 40 extra grams of agent). It is remarkable that the filling procedure still yielded final agent/N<sub>2</sub> masses within  $\pm 10\%$ . The extra liquid vaporized at the elevated temperature.

**6.1.3.1 FTIR Spectra.** The spectra taken before and after the storage period were examined to identify changes in the gas phase. Any new peaks observed in the spectra taken after storage would indicate that some degradation of the agent had occurred during the storage time. In addition a decrease in the area under specific peaks of the final spectra would indicate degradation. Equation 1 would yield quantitative concentrations.

Figures 2-4 show the initial and final overlaid IR spectra for three of the agents. In some of the spectra, baseline perturbations can be seen. However, these perturbations generally occur above 2500 cm<sup>-1</sup> outside the area of interest for fluorinated compounds and are likely due to detector sensitivity fall off or gas cell window contamination.

For all thirteen agents examined, no new peaks were observed in any of the spectra. Peaks of new compounds could be masked by the peaks formed by the original compound, so examination of the peak heights or areas under the peaks would provide further validation of whether or not the agents were stable.

During the course of the storage experiments, the FTIR system experienced a catastrophic failure of the computer. The FTIR was updated with new computer hardware, but several electronic files were lost which included the initial and final spectra for the agents HCFC-22, HCFC-124, HFC-125,

Table 2. Agent and Metal Amounts in Storage Cylinders for Stability Under Storage Tests

Agent: HCFC-22

Metal	Metal Mass ( $\pm 0.01$ g)	Agent		Agent/N <sub>2</sub>		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.1$ g)
304 stainless steel	272.07	0.97	40	4.13	75.6	74.8
Nitronic-40 (21-6-9)	325.45	0.97	40	4.13	72.8	73.0
Inconel 625	320.29	0.97	40	4.13	75.4	75.2
6061-T6 aluminum	96.55	0.97	40	4.13	76.8	75.5
4130 alloy steel	304.45	0.95	39	4.17	76.5	75.0
AM 350 stainless	285.68	0.94	39	4.13	-- <sup>a</sup>	77.1
Cu/Be C82500	311.20	0.96	39	4.17	77.8	76.6
13-8 Mo stainless	280.13	0.95	39	4.13	74.6	73.5

Agent: HCFC-124

Metal	Metal Mass ( $\pm 0.01$ g)	Agent		Agent/N <sub>2</sub>		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.1$ g)
304 stainless steel	272.61	0.31	19	4.13	--	--
Nitronic-40 (21-6-9)	323.56	0.31	19	4.20	63.1	63.1
Inconel 625	319.78	0.33	20	4.15	62.9	63.3
6061-T6 aluminum	96.95	0.31	19	4.13	64.8	63.8
4130 alloy steel	303.52	0.33	20	4.13	63.5	63.6
AM 350 stainless	283.72	0.33	20	4.17	62.8	51.3
Cu/Be C82500	311.48	0.33	20	4.17	65.3	63.2
13-8 Mo stainless	285.73	0.31	19	4.17	64.2	64.6

<sup>a</sup> -- data not available



Table 2. (continued) Agent and Metal Amounts in Storage Cylinders for Stability Under Storage Tests

Agent: HFC-125

Metal	Metal Mass ( $\pm 0.01$ g)	Agent		Agent/N <sub>2</sub>		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.1$ g)
304 stainless steel	273.08	0.69	38	4.20	72.1	72.7
Nitronic-40 (21-6-9)	323.72	0.69	38	4.20	74.4	74.2
Inconel 625	320.11	0.69	38	4.20	74.1	74.4
6061-T6 aluminum	96.87	0.69	38	4.20	76.5	76.7
4130 alloy steel	303.57	0.69	38	4.20	73.4	73.6
AM 350 stainless	286.23	0.69	38	4.20	76.0	45.5
Cu/Be C82500	311.06	0.72	39	4.20	76.9	77.2
13-8 Mo stainless	283.45	0.69	38	4.20	72.6	73.2

Agent: HFC-32/HFC-125

Metal	Metal Mass ( $\pm 0.01$ g)	Agent		Agent/N <sub>2</sub>		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.1$ g)
304 stainless steel	273.49	0.69	24	4.20	55.2	55.4
Nitronic-40 (21-6-9)	323.03	0.69	24	4.20	55.2	55.7
Inconel 625	320.34	0.69	24	4.20	53.9	54.7
6061-T6 aluminum	96.72	0.69	24	4.20	55.2	55.4
4130 alloy steel	303.44	0.69	24	4.20	55.7	56.1
AM 350 stainless	286.22	0.69	24	4.20	55.6	55.7
Cu/Be C82500	311.02	0.69	24	4.20	58.1	58.3
13-8 Mo stainless	284.32	0.69	24	4.20	55.2	56.0

Table 2 (continued). Agent and Metal Amounts in Storage Cylinders for Stability Under Storage Tests

Agent: HFC-134a

Metal	Metal Mass ( $\pm 0.01$ g)	Agent		Agent/N <sub>2</sub>		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.01$ g)
304 stainless steel	273.60	0.59	27	4.20	66.8	66.6
Nitronic-40 (21-6-9)	324.52	0.59	27	4.20	62.3	60.1
Inconel 625	319.85	0.59	27	4.20	64.2	63.6
6061-T6 aluminum	96.83	0.59	27	4.41	68.3	67.9
4130 alloy steel	303.77	0.59	27	4.20	64.1	63.9
AM 350 stainless	284.73	0.59	27	4.20	66.7	66.9
Cu/Be C82500	311.65	0.59	27	4.20	62.2	61.6
13-8 Mo stainless	285.24	0.59	27	4.20	64.2	64.3

Agent: FC-218

Metal	Metal Mass ( $\pm 0.01$ g)	Agent		Agent/N <sub>2</sub>		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.1$ g)
304 stainless steel	274.10	0.81	80.1	4.24	107.7	107.3
Nitronic-40 (21-6-9)	324.78	0.79	78.7	4.24	104.7	104.2
Inconel 625	317.72	0.79	78.7	4.24	107.1	107.1
6061-T6 aluminum	97.01	0.79	78.7	4.24	107.2	107.2
4130 alloy steel	303.34	0.79	78.7	4.24	101.1	102.1
AM 350 stainless	284.92	0.79	78.7	4.24	101.9	105.9
Cu/Be C82500	311.66	0.79	78.7	4.24	103.7	103.6
13-8 Mo stainless	282.99	0.76	75.3	4.28	--	83.4

Table 2 (continued). Agent and Metal Amounts in Storage Cylinders for Stability Under Storage Tests

Agent: HFC-227

Metal	Metal Mass ( $\pm 0.01$ g)	Agent		Agent/N <sub>2</sub>		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.1$ g)
304 stainless steel	272.8	0.40	31	4.26	72.8	73.0
Nitronic-40 (21-6-9)	323.29	0.40	31	4.20	71.6	71.5
Inconel 625	318.02	0.41	32	4.20	69.6	70.3
6061-T6 aluminum	97.02	0.41	32	4.20	69.7	69.7
4130 alloy steel	303.18	0.40	31	4.20	66.4	66.5
AM 350 stainless	285.37	0.40	31	4.20	70.0	69.9
Cu/Be C82500	310.51	0.41	32	4.24	70.2	70.0
13-8 Mo stainless	282.26	0.40	31	4.24	68.5	68.5

Agent: FC-31-10

Metal	Metal Mass ( $\pm 0.01$ )	Agent		Agent/N <sub>2</sub>		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.1$ g)
304 stainless steel	273.79	0.23	24	4.20	97.7	97.8
Nitronic-40 (21-6-9)	325.27	0.21	22	4.20	103.4	103.3
Inconel 625	320.01	0.21	22	4.20	111.9	112.4
6061-T6 aluminum	97.03	0.21	22	4.20	117.1	100.4
4130 alloy steel	302.73	0.21	22	4.20	113.6	111.9
AM 350 stainless	287.56	0.21	22	4.20	106.4	106.4
Cu/Be C82500	311.62	0.21	22	4.20	110.9	110.9
13-8 Mo stainless	284.99	0.21	22	4.20	110.8	110.3

Table 2. (continued) Agent and Metal Amounts in Storage Cylinders for Stability Under Storage Tests

Agent: FC-116

Metal	Metal Mass ( $\pm 0.01$ g)	Agent		Agent/N <sub>2</sub>		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.1$ g)
634 stainless steel	273.23	0.55	32.4	4.20	66.4	66.0
Nitronic-40 (21-6-9)	324.53	0.55	32.4	4.20	68.7	68.6
Inconel 625	320.85	0.56	33.2	4.20	71.2	71.4
6061-T6 aluminum	97.01	0.56	33.2	4.20	71.8	71.6
4130 alloy steel	304.05	0.56	33.2	4.27	72.2	71.8
AM 350 stainless	286.24	0.56	32.8	4.20	72.7	72.6
Cu/Be C82500	311.97	0.57	33.6	4.22	47.5	47.2
13-8 Mo stainless	281.79	0.57	33.6	4.21	70.8	70.6

Agent: FC-318

Metal	Metal Mass ( $\pm 0.01$ g)	Agent		Agent/N <sub>2</sub>		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.1$ g)
304 stainless steel	272.47	0.26	23.4	4.20	66.3	66.3
Nitronic-40 (21-6-9)	324.44	0.26	23.4	4.20	65.6	65.4
Inconel 625	319.30	0.25	22.7	4.20	66.5	66.3
6061-T6 aluminum	69.55	0.25	22.7	4.22	67.0	66.9
4130 alloy steel	303.38	0.26	23.4	4.20	60.5	60.6
AM 350 stainless	284.62	0.25	22.7	4.20	64.5	64.5
Cu/Be C82500	313.05	0.26	23.4	4.20	64.2	63.9
13-8 Mo stainless	281.84	0.25	22.7	4.22	65.6	65.4

Table 2 (continued). Agent and Metal Amounts in Storage Cylinders for Stability Under Storage Tests

Agent: HFC-236

Metal	Metal Mass ( $\pm 0.01$ g)	Agent		Agent/N <sub>2</sub>		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.1$ g)
304 stainless steel	274.32	0.26	18	4.20	57.1	57.1
Nitronic-40 (21-6-9)	325.85	0.25	17	4.20	58.0	58.0
Inconel 625	320.19	0.26	18	4.21	58.2	58.3
6061-T6 aluminum	97.18	0.25	17	4.20	57.8	57.8
4130 alloy steel	302.58	0.25	17	4.22	57.0	57.2
AM 350 stainless	283.61	0.25	17	4.22	58.4	58.7
Cu/Be C82500	311.32	0.24	16	4.20	57.6	57.8
13-8 Mo stainless	283.96	0.24	16	4.21	56.6	56.6

Agent: halon 1301

Metal	Metal Mass ( $\pm 0.01$ g)	Agent		Agent/N <sub>2</sub>		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.1$ g)
304 stainless steel	272.72	1.46	113	4.22	128.3	--
Nitronic-40 (21-6-9)	324.55	1.46	113	4.24	142.6	142.7
Inconel 625	318.41	1.45	112	4.27	143.3	143.6
6061-T6 aluminum	97.73	1.41	109	4.24	141.0	141.2
4130 alloy steel	301.56	1.36	102	4.13	141.3	141.3
AM 350 stainless	284.83	1.34	101	4.19	136.6	136.8
Cu/Be C82500	323.26	1.32	99	4.15	137.1	137.4
13-8 Mo stainless	289.68	1.32	99	4.19	134.3	134.5

Table 2 (continued). Agent and Metal Amounts in Storage Cylinders for Stability Under Storage Tests

Agent:  $\text{CF}_3\text{I}$ 

Metal	Metal Mass ( $\pm 0.01$ g)	Agent		Agent/ $\text{N}_2$		
		Pressure ( $\pm 0.02$ MPa)	Mass (g)	Pressure ( $\pm 0.02$ MPa)	Mass Before Storage ( $\pm 0.1$ g)	Mass After Storage ( $\pm 0.1$ g)
304 stainless steel	271.69	0.34	30	4.20	71.5	71.2
Nitronic-40 (21-6-9)	324.22	0.34	30	4.20	70.4	70.4
Inconel 625	318.68	0.34	30	4.20	66.5	66.5
6061-T6 aluminum	98.99	0.34	30	4.20	69.3	67.0
4130 alloy steel	300.22	0.34	30	4.20	71.7	71.8
AM 350 stainless	286.06	0.34	30	4.20	71.3	52.4
Cu/Be C82500	323.63	0.34	30	4.20	73.8	72.9
13-8 Mo stainless	297.59	0.34	30	4.20	71.2	71.6

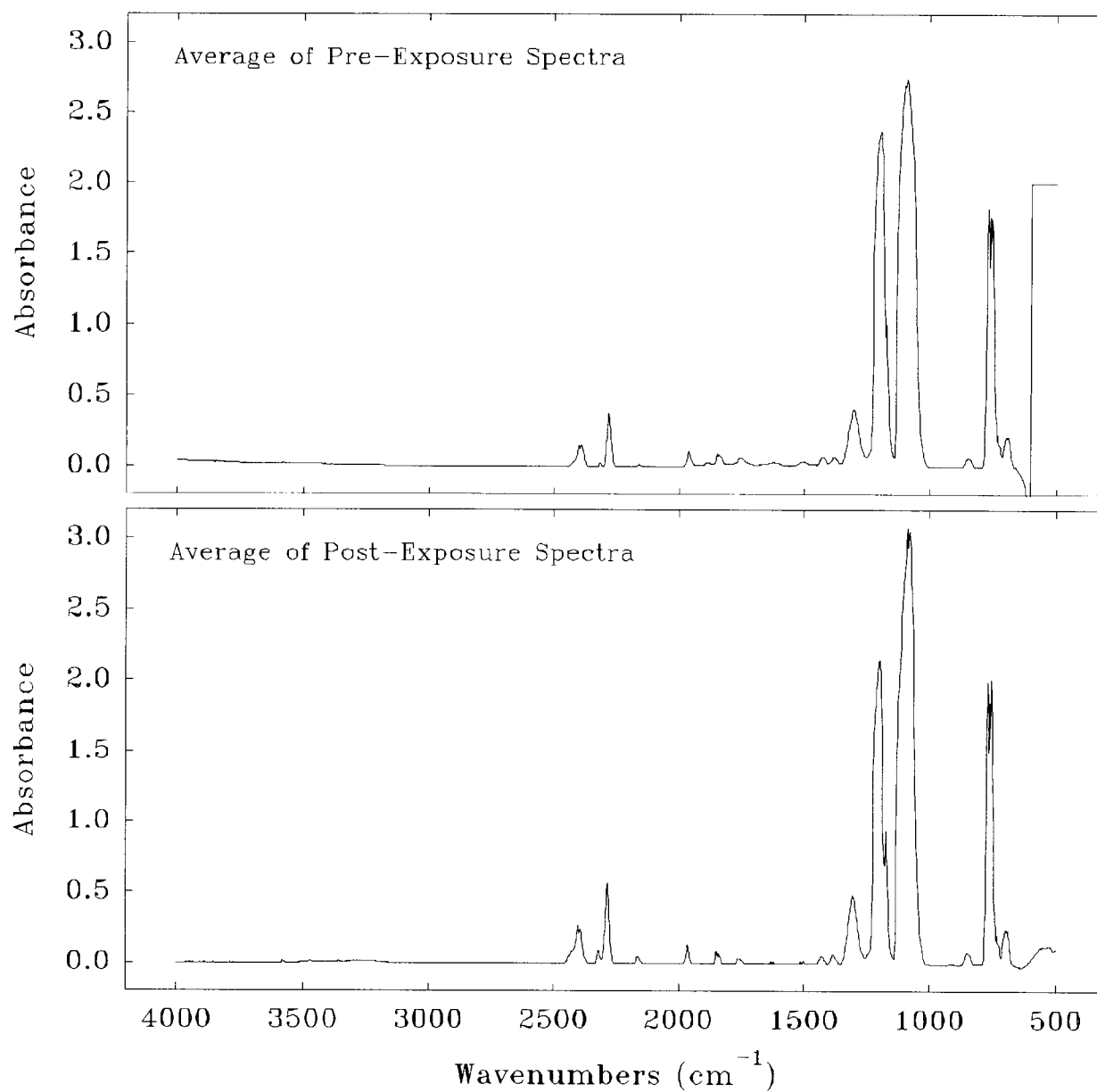


Figure 2. Pre- and post-storage spectra for halon 1301.

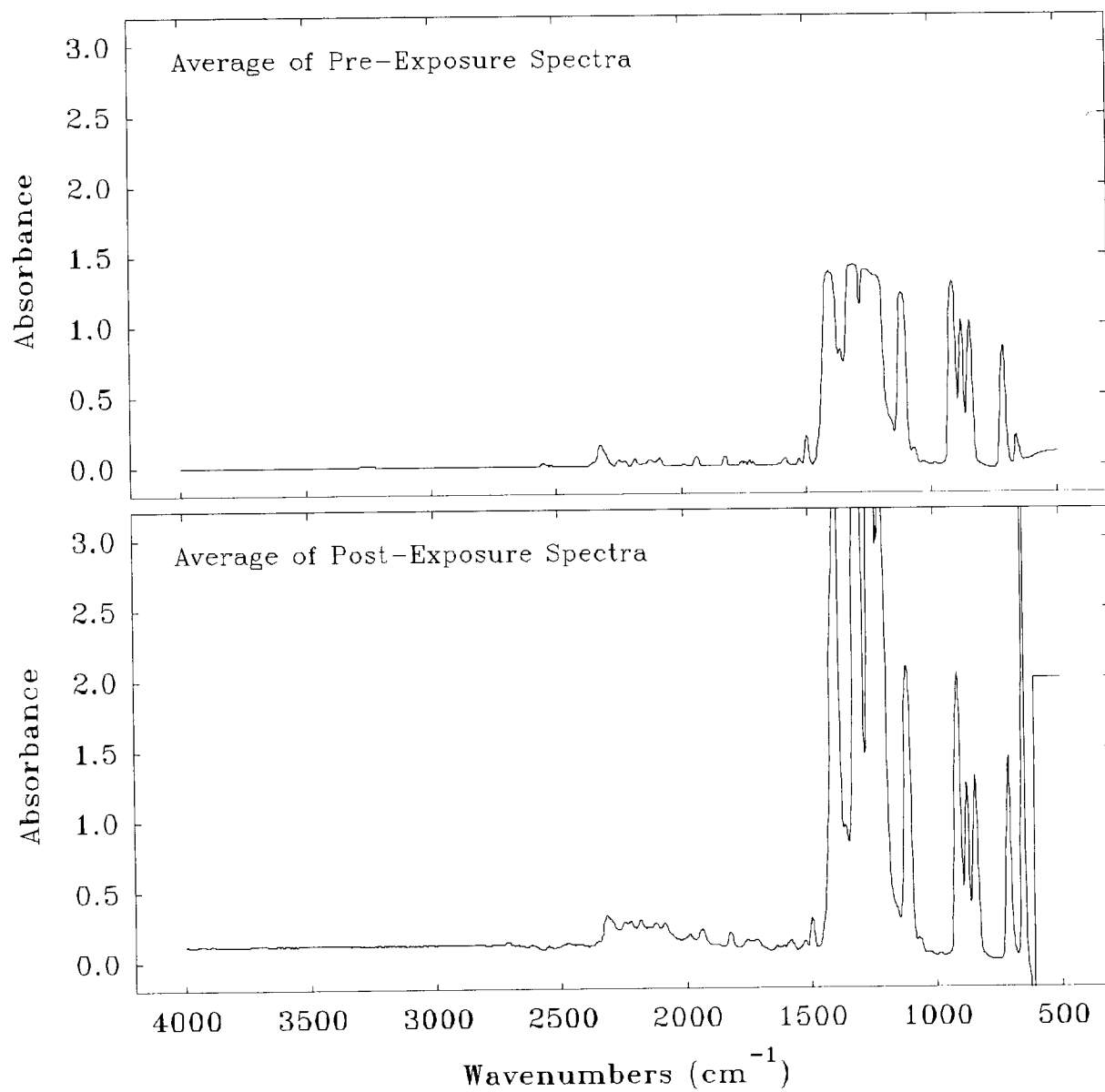


Figure 3. Pre- and post-storage spectra for HFC-236.



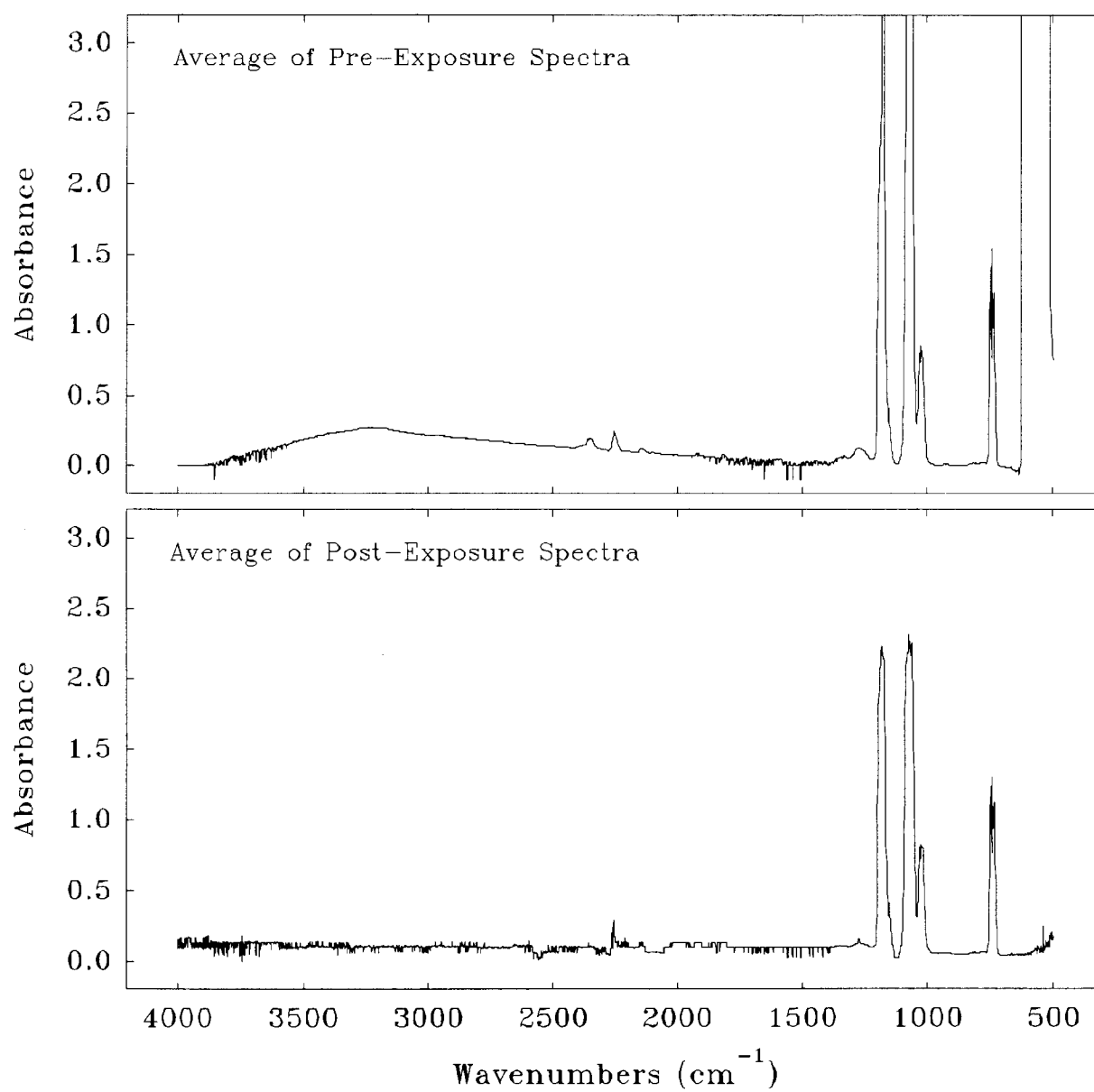


Figure 4. Pre- and Post-storage spectra for CF<sub>3</sub>I.

and HFC-32/HFC-125. Therefore no peak areas are available for those agents. Judgment for these agents were based on inspection of the hard-copy plots of the spectra.

Selected peaks in the spectra before and after the 28 day storage were integrated for the remaining agents. Table 3 lists the initial and final integrated areas of selected peaks for halon 1301, HFC-236, and  $\text{CF}_3\text{I}$ . The integrated peaks were selected on the basis of the following criteria to ensure possible absorbance linearity:

- an absorbance of  $< 1$
- acceptable baseline resolution
- wave number greater than  $700\text{ cm}^{-1}$

For halon 1301, there was a tendency for the peak areas to increase, whereas for  $\text{CF}_3\text{I}$  there was a tendency for the peak areas to decrease. The experiments are very repeatable within a short time span (as indicated by the small uncertainties for each agent-metal combination). Over longer time periods, alignment of the FTIR becomes critical and the comparison of initial and final spectra can be expected to have a larger uncertainty. Thus, the key indicator of degradation should be taken as the formation of new compounds evidenced in the spectra. No new compounds were identified in any of the spectra for any of the agents. For  $\text{CF}_3\text{I}$ , an initial spectra and two final spectra were available (one taken after eight days of storage and one after the full 28 day exposure). The peak areas systematically decreased over the four week exposure, but the change may be within the experimental measurement error. Since no new compounds were observed in the  $\text{CF}_3\text{I}$  spectra, the possible degradation of  $\text{CF}_3\text{I}$  deserves further examination and will be included in the forthcoming longer term studies.

**6.1.3.2 Examination of Metals.** The metals were removed from the cylinders, examined, and then wrapped in aluminum foil for later reference. Changes in the appearance of the metals are given in Table 4. When the metals from the  $\text{CF}_3\text{I}$  cylinders were removed, a dark solid was apparent on the coupons, then disappeared within seconds. The solid may have been  $\text{I}_2$  which then sublimed to gaseous  $\text{I}_2$ . For the other metals, visual changes may be due to the prolonged heating of the metal or by interaction with the agent. For the former, effects would be observed for all of the agents (for example, the Cu/Be C82500 coupons). Interaction with the agents is far more common, with some metals affected by only a few agents and others effected by nearly all of the agents. HCFC-22 and  $\text{CF}_3\text{I}$  affected most of the metals, while for others, only the Cu/Be C82500 coupons were affected.

## 6.2 Agent Residue Study

The objective of this phase of the project was to determine if the agents as received contained measurable contamination that might have an effect on the results of our experiments. An attempt was made to determine high volatile residue contaminants as well as low volatile residue contaminants. If a residue was discovered some effort was made to determine the source of the contamination.

**6.2.1 Experimental Method.** The apparatus used for determining residue is shown in Figure 5. The cylinders as received were fitted with hardware that allowed them to be connected to the copper cooling coil with a commercially available flexible hose commonly used in the refrigerant industry. Graduated tubes of *ca.* 2 ml capacity (the bottoms of larger graduated centrifuge tubes) were used to

Table 3. Initial and Final Integrated Areas of Selected Peaks in the IR Spectra of Halon 1301

Metal	Band (cm <sup>-1</sup> )	Integrated Area		c <sub>f</sub> /c <sub>i</sub>
		Initial	Final	
304 stainless steel	1351.85-1259.28	15.45±0.01	17.49±0.01	1.13
Nitronic 40 (21-6-9)	"	15.56±0.02	18.32±0.02	1.18
Inconel 625	"	15.72±0.02	18.55±0.04	1.18
6061-T6 aluminum	"	15.90±0.02	19.80±0.66	1.25
4130 alloy steel	"	15.32±0.04	18.46±0.04	1.20
AM 350 stainless	"	15.14±0.03	18.44±0.04	1.22
Cu/Be C82500	"	15.24±0.03	18.61±0.03	1.22
13-8 Mo stainless	"	14.98±0.05	17.51±0.11	1.17
304 stainless steel	1984.39-1928.46	1.88±0.01	2.08±0.02	1.11
Nitronic 40 (21-6-9)	"	1.90±0.01	2.16±0.02	1.14
Inconel 625	"	1.95±0.01	2.21±0.01	1.13
6061-T6 aluminum	"	1.95±0.02	2.35±0.07	1.21
4130 alloy steel	"	1.88±0.02	2.18±0.01	1.16
AM 350 stainless	"	1.87±0.01	2.18±0.01	1.17
Cu/Be C82500	"	1.89±0.01	2.23±0.02	1.18
13-8 Mo stainless	"	1.85±0.02	2.11±0.01	1.14
304 stainless steel	2302.58-2250.52	7.90±0.03	8.20±0.08	1.04
Nitronic 40 (21-6-9)	"	7.92±0.10	8.63±0.10	1.09
Inconel 625	"	8.10±0.05	8.80±0.02	1.09
6061-T6 aluminum	"	8.10±0.03	9.30±0.25	1.15
4130 alloy steel	"	7.78±0.01	8.64±0.03	1.11
AM 350 stainless	"	7.77±0.04	8.74±0.06	1.12
Cu/Be C82500	"	7.82±0.01	8.88±0.12	1.14
13-8 Mo stainless	"	7.65±0.04	8.41±0.05	1.10

Table 3, (continued). Initial and Final Integrated Areas of Selected Peaks in the IR Spectra of  $\text{CF}_3\text{I}$ .

Metal	Band ( $\text{cm}^{-1}$ )	Integrated Area		$c_f/c_i$
		Initial	Final	
Blank	1312.32±1225.54	3.55±0.02	3.30±0.01	0.93
304 stainless steel	"	3.77±0.02	3.60±0.03	0.95
Nitronic 40 (21-6-9)	"	3.55±0.03	3.47±0.05	0.98
Inconel 625	"	3.63±0.01	3.26±0.01	0.90
6061-T6 aluminum	"	3.68±0.01	3.56±0.01	0.97
4130 alloy steel	"	3.70±0.02	3.46±0.03	0.94
AM 350 stainless	"	3.27±0.02 <sup>a</sup>	3.35±0.04	1.02
Cu/Be C82500	"	3.69±0.01	3.69±0.04	1.00
13-8 Mo stainless	"	3.48±0.03	3.39±0.02	0.97
Blank	762.70-717.38	27.02±0.12	22.63±0.04	0.84
304 stainless steel	"	29.03±0.08	24.38±0.13	0.84
Nitronic 40 (21-6-9)	"	27.18±0.23	23.75±0.04	0.87
Inconel 625	"	27.58±0.03	22.54±0.04	0.82
6061-T6 aluminum	"	28.21±0.13	24.07±0.05	0.85
4130 alloy steel	"	27.99±0.12	23.47±0.03	0.84
AM 350 stainless	"	24.69±0.12 <sup>a</sup>	22.95±0.10	0.93
Cu/Be C82500	"	27.64±0.27	24.66±0.01	0.89
13-8 Mo stainless	"	26.13±0.27	22.99±0.02	0.88

<sup>a</sup> - Outliers

Table 3, (continued). Initial and Final Integrated Areas for Selected Peaks in the IR Spectra of HFC-236

Metal	Band (cm <sup>-1</sup> )	Integrated Area		c <sub>f</sub> /c <sub>i</sub>
		Initial	Final	
304 stainless steel	1508.06-1473.34	3.71 <sup>a</sup>	4.29±0.09	1.16
Nitronic 40 (21-6-9)	"	3.68±0.23	4.65 <sup>a</sup>	1.26
Inconel 625	"	3.78±0.24	4.77 <sup>a</sup>	1.26
6061-T6 aluminum	"	3.66±0.14	3.37±0.01	0.92
4130 alloy steel	"	3.78±0.33	3.15±0.01	0.83
AM 350 stainless	"	3.65±0.14	3.27±0.01	0.90
Cu/Be C82500	"	3.62±0.10	3.28±0.01	0.91
13-8 Mo stainless	"	3.70±0.26	3.28±0.01	0.89
304 stainless steel	1843.61-1799.25	2.16 <sup>a</sup>	2.30±0.04	1.06
Nitronic 40 (21-6-9)	"	2.09±0.14	2.42 <sup>a</sup>	1.16
Inconel 625	"	2.11±0.15	2.45 <sup>a</sup>	1.16
6061-T6 aluminum	"	2.03±0.08	1.93±0.01	0.95
4130 alloy steel	"	2.09±0.20	1.82±0.06	0.87
AM 350 stainless	"	2.00±0.09	1.82±0.01	0.91
Cu/Be C82500	"	1.97±0.06	1.84±0.01	0.93
13-8 Mo stainless	"	2.02±0.15	1.83±0.03	0.91

<sup>a</sup> - Only two usable spectra

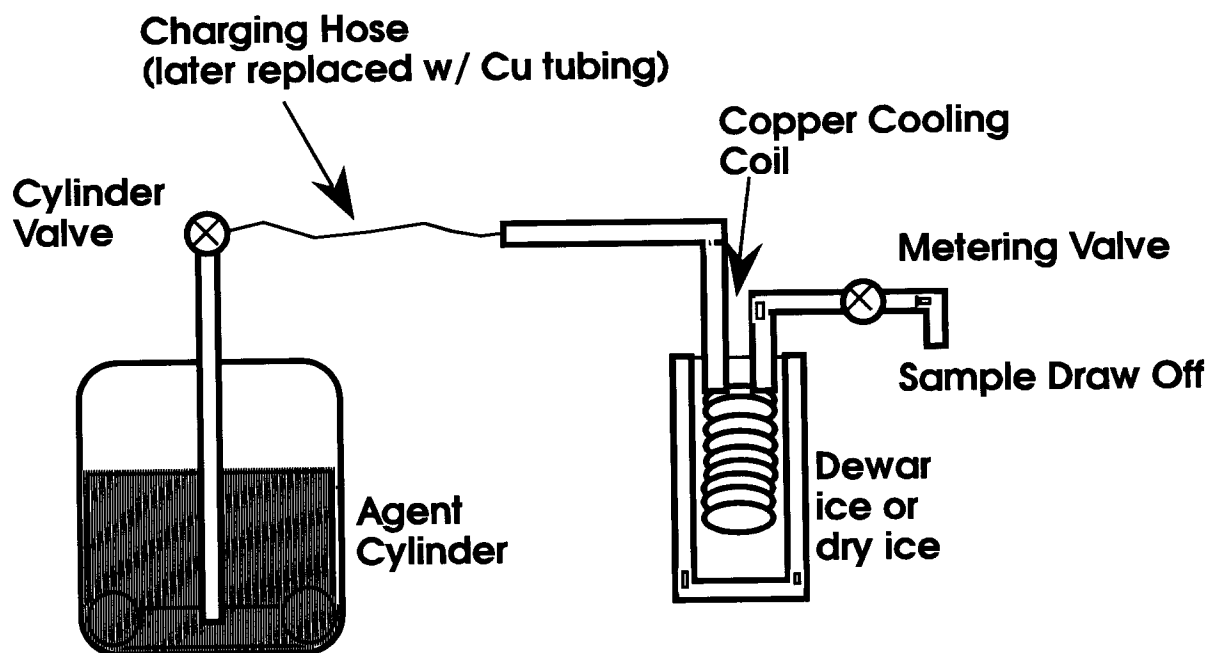


Figure 5. Apparatus for determining agent residue.

collect 1 ml of liquid agent. All tubes were dried at 105 °C for one hour, kept in a desiccator, then weighed with an analytical balance with 0.1 mg accuracy before filling. Three tubes were used to collect each agent. After the 1 ml samples were collected, the tubes were kept in an ice or dry ice

Table 4. Visible Changes in Metals After 28 Day Exposure at 149°C (300°F)

Agent	304 stainless steel	Nitronic-40 (21-6-9)	Inconel 625	6061-T6 aluminum	4130 alloy steel	AM 350 stainless	Cu/Be C82500	13-8 Mo stainless
HCFC-22	✓ <sup>a</sup>	✓	✓	✓	✓		✓	✓
HCFC-124							✓	
HFC-125							✓	
HFC-32/HFC-125							✓	
HFC-134a					✓		✓	
FC-218		✓		✓	✓		✓	
HFC-227					✓		✓	
FC-31-10		✓		✓	✓		✓	✓
FC-116					✓		✓	
FC-318	✓				✓		✓	
HFC-236							✓	
halon 1301							✓	
CF <sub>3</sub> I	✓	✓	-- <sup>b</sup>	✓	✓	✓	--	✓

a - ✓ indicates visible change in metal appearance after exposure

b - data not available

bath (depending on the boiling point of the agent) to allow controlled evaporation. When all of the agent had evaporated, the tubes were then placed in a desiccator for at least one hour and weighed on the previously described balance.

Agents with a boiling point greater than -26 °C were processed with the cooling coil immersed in ice and the tubes evaporated in ice. Those agents with a boiling point less than -39 °C required dry ice and acetone in the dewar holding the cooling coil and controlled evaporation of the tubes in a tray containing dry ice. All agents with the exception of FC-116, which is a gas at room temperature, were removed from the cylinders as a liquid and collected in the graduated tubes as a liquid. The FC-116 condensed in the cooling coil and was collected as a liquid.

An effort was made to determine the presence of highly volatile residues when the graduated tubes were at low temperature after filling and during the controlled evaporation. The formation of frost prevented any clear observation of the presence of residue.

If measurable residue was present in the graduated tubes after the agents had boiled away and a weighing at ambient was done, the tubes were then heated to 150 °C for one hour, cooled to ambient in a desiccator, and reweighed.

**6.1.2 Results of residue analyses.** Initially, the residue analysis was performed on several of the agents contained in 1000 ml cylinders. These agents were prepared in small laboratory quantities and no measurable residues were detected. A representative of the manufacturer of these agents indicated that no low volatile residues should be present because they are distilled prior to filling and are of high purity.

As production and pilot quantities were received, the residue analysis was performed. Initially, the HCFC-22 and HCFC-124 samples were found to have as much as 1.3 and 0.3 %, respectively, of a yellow, oily residue. The residue was still visible when the tubes were heated to 150 °C, however, the amount was reduced to 0.9 and less than 0.1 %, respectively. The manufacturer of these agents was contacted with a lot number from the HCFC-22. One of their research chemists contacted the plant where this agent had been filled and found that the 13.6 kg non-returnable cylinders do contain a small amount of oil to protect the inner walls. Since many of the applications of HCFC-22 require the addition of oil to the agent, no effort was made to remove the oil. In later discussions with another representative of the manufacturer, this statement was said to be incorrect.

If left in the high pressure flexible filling lines commonly used by the refrigeration industry (and used to connect the cylinders to the cooling coil in our experiments), interaction between HCFC-22 and HCFC-124 and the black, rubber lining resulted in a yellow, oily residue. If the connection from the cylinder to the cooling coil was made with a metal tube such as copper, no significant residue was collected. This dissolution or extraction phenomenon was only seen with HCFC-22 and HCFC-124, which also contain chlorine.

Table 5 summarizes the results of the low volatile residue analyses for all agents, except FC-318 and CF<sub>3</sub>I. There was some uncertainty in the weighing of the tubes after they were conditioned to ambient temperature in the desiccator and weighed. In some cases, the weight after collection was actually slightly less than the initial weight. In the table, a report of a trace amount indicates that the tubes showed less than 1 mg of residue. Only the HFC-134a and HFC-236 contained low volatile residues greater than 1 mg and the weight increase was consistent for the three tubes.

## 6.3 Conclusions

- No new compounds, observable above the background, were evident after 28 day, 150 °C exposure of any of the candidate agents.
- A possible decrease in integrated areas for selected spectral peaks was observed only for CF<sub>3</sub>I. This observation may be within the experimental error, and was without accompanying formation of new compounds. An observation of a dark solid on metal coupons post-exposure for this agent may have been I<sub>2</sub> which could result from either degradation or impurity in the original agent. Longer term study is warranted for this agent.



Table 5. Low Volatile Residue Results

Agent	Weight % Residue
HCFC-22	Trace
HCFC-124	Trace
HFC-134a	< 0.1
HFC-125	Trace
HFC-32/HFC-125	Trace
HFC-227	Trace
FC-31-10	Trace
HFC-236	0.2
FC-116	Trace
FC-218	Trace
FC-318	Not Measured
CF <sub>3</sub> I	Not Measured

- All agents except HFC-134a and HFC-236 appeared to be relatively free of low volatile residues. The small amounts detected for the two agents appeared to be oily and might have come from the container walls.
- For the chemicals studied, stability in long-term storage and agent residue should not be major deciding factors in determining selection of appropriate agents for further study. As noted above, CF<sub>3</sub>I could be an exception.

## 6.4 References

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